

# PATENT SPECIFICATION

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## (54) PROCESS FOR PREPARING ADDITIVES

(71) We, MOBIL OIL CORPORATION, a corporation organised under the laws of the State of New York, United States of America, of 150 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel compositions of matter and their preparation. Additionally, this invention relates to the use of these novel compositions of matter as engine oil additives.

A great deal of effort is being directed to providing a lubricant which will permit present-day automotive engines to be operated at a high level of efficiency over long periods of time. A difficulty arises because lubricating oils tend to deteriorate under the conditions of use, with attendant formation of sludge, lacquer and resinous materials which adhere to the engine parts, thereby lowering the operating efficiency of the engine. To counteract the formation of these deposits, certain chemical additives have been found which, when added to lubricating oils, have the ability to keep the deposit-forming materials suspended in the oil, so that the engine is kept clean and in efficient operating condition for extended periods of time. These added agents are known in the art as detergents or dispersants.

Metal-containing organic compounds are particularly useful as additives in this respect. However, the troublesome deposits which form on the skirt of the piston and on the walls of the combustion chamber, as well as on valves and spark plugs are also partially attributable to these metal containing additives employed in the lubricant. Whenever oil is burned in the engine, as occurs with the oil film present in the cylinder wall during the combustion stroke, many metal-containing additives present in the oil may form an ash which is partially deposited on the various surfaces of the combustion chamber and on those of the spark plugs and valves.

Accordingly, it is an object of this invention to provide novel compositions of matter which are metal- or mineral-free detergents or dispersants for lubricants.

Several known non-metallic detergents have previously been used in lubricating compounds. However, they have not proved to be entirely satisfactory. Several additives which are particularly effective are based upon condensation products of an hydroxyaromatic, an aldehyde and an amine, the so-called Mannich reaction. These additives are multi-functional improvers especially adapted for mineral oils and as pour depressants therein. These compounds have also been recognized as exhibiting detergent properties. Hydroxyaromatic compounds which are substituted by a short chain alkyl group or by relatively high molecular weight straight chain chlorinated aliphatic hydrocarbons are also suitable for condensation products with aldehydes and amines.

U.S. Patent No. 2,868,823, for example, describes the preparation of short-chain substituted phenols using an aluminum complex catalyst. The chain lengths of the polyalkylene substituents are, however, too short for the products to be satisfactory as additives.

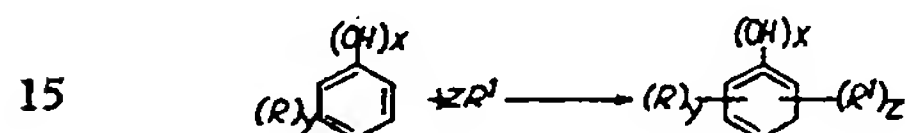
U.S. Patent No. 2,655,544 also describes the preparation of alkylated phenols, although here again the alkyl substituents do not have a sufficiently long chain length for the products to be satisfactory additives. In addition, the use of boron trifluoride as a catalyst is recommended. We have found that gaseous boron trifluoride is an unsatisfactory catalyst, giving, as it does, a very low yield.

Other earlier attempts to prepare alkylated phenols are described in U.S. Patents Nos. 2,916,524 and 2,698,867. U.S. Patent No. 2,916,524 describes the use of a polybutyl rubber to produce a butylated phenol, but the chain lengths of the products are too short for satisfactory use as additives. U.S. Patent No. 2,698,867 describes the use of a hydrogen fluoride catalyst, but this again does not give a satisfactory product.

We have now found that very good additives can be produced by reacting a high molecular

weight polyalkylene compound with a phenolic compound in the presence of a boron trifluoride complex catalyst. The complex catalyst gives results which are far superior to those obtained with gaseous boron trifluoride. This is quite unexpected because normally the complex would be expected to act in the same way as the gas.

The additives of this invention are made by reacting (1) a phenolic compound with (2) a high molecular weight polyalkylene compound with a molecular weight of 600 to 3000, preferably 750 to 1200. The reaction involved may be depicted as follows:



wherein, R is a hydrocarbon or substituted-hydrocarbon radical, R' is a polyalkylene compound where the repeating alkylene unit may be from C<sub>3</sub> to C<sub>8</sub>, x is 1 or 2, y is 0, 1 or 2 and z is 1 or 2. According to infrared spectroscopy, the final product is a mixture of orthopara- and 2, 4-substituted phenol. The present invention is further predicated upon the discovery that these additives will improve lubricants by exhibiting high dispersant properties therein.

According to the present invention a hydrocarbon composition comprises a hydrocarbon vehicle and from 0.05 to 25% by weight of an aforesaid additive.

Representative high molecular weight alkyl substituted phenols contemplated by the present invention are polypropenylphenol, polybutenylphenol, polypentenylphenol and similarly substituted phenols. For example, in place of the phenol, high molecular weight alkyl substituted compounds of resorcinol, hydroquinone, catechol, cresol, xylene, hydroxydiphenol, benzylphenol, phenylethylphenol, phenol resins, methylhydroxydiphenyl, guaiacol, alpha and beta naphthol, alpha and beta methylnaphthol, tolylnaphthol, xylylnaphthol, benzylnaphthol, anthranol, phenylmethylnaphthol, phenanthrol, monomethyl ether of catechol, phenoxyphenol, chlorophenol, phenol sulfides and the like may be used.

The polyalkenyl phenols of this invention are preferably made by reacting 0.1 to 10 moles of a phenol with 1 mole of a polyalkylene in the presence of a boron trifluoride complex catalyst, such as the etherate, phenolate or phosphate complexes. The reaction is normally conducted at a temperature of 80° to 250°C. This process is particularly effective when conducted by reacting 1 to 1.5, or especially 1.25 moles, of phenol to 1 mole of a polyalkylene compound in the presence of a BF<sub>3</sub> phenolate at about 150°C. The product is conveniently dissolved in an aromatic

solvent and then washed with water to remove unreacted components. Upon filtration and removal of the aromatic solvent by distillation; the product, a clear, viscous oil, remains.

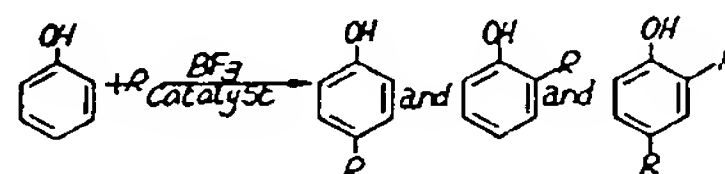
The invention in several particular embodiments is illustrated by the following examples, wherein amounts and percentages are on a weight basis unless indicated otherwise.

#### EXAMPLE 1

This example illustrates the alkylation of phenol with polypropylene which gives polypropenylphenol using 2.5% BF<sub>3</sub> as a catalyst. Materials:

860 g. (1 mol) polypropylene (M.W. cryoscopic 860)  
117.5 (1 mol+25% xs) phenol (66.5 g from the phenolate complex)  
90.5 g. BF<sub>3</sub>·2C<sub>6</sub>H<sub>5</sub>OH 26% BF<sub>3</sub> (24 g. BF<sub>3</sub> and 66.5 g. Phenol)

The BF<sub>3</sub> content of the catalyst was 2.5% of the total amount of reactants.



R=polypropylene

The apparatus consisted of a 3 liter, four-necked reaction flask equipped with a mechanical stirrer, reflux condenser, thermometer and dropping funnel.

The polypropylene and phenol (51 g.) were charged to the flask at a temperature of 60°C. and the BF<sub>3</sub>·2C<sub>6</sub>H<sub>5</sub>OH complex (24 g. BF<sub>3</sub> and 66.5 g. phenol) was added dropwise through the dropping funnel during continuous stirring. The reaction mixture was heated at 80°C. for 3 hours, at 100°C. for 5 more hours, then it was dissolved in 500 cc toluene and washed with hot water to remove the BF<sub>3</sub> and unreacted phenol, until neutral to litmus. The solution was filtered and the toluene was distilled off under vacuum up to 175°C. The product, a clear brown, viscous oil gave the following analysis:

	Theory	Found
Active Hydrogen (Zerevitinov determination)	1.05 m moles CH <sub>4</sub> /g	1.07 m moles CH <sub>4</sub> /g

Chromatographic separation of the aromatics from the non-aromatics through Attapulugus clay (Fuller's earth) gave an alkylation yield of 59.1%.

#### EXAMPLE 2

This example illustrates the alkylation of phenol with polypropylene which gives poly-

propenylphenol using 0.5%  $\text{BF}_3$  as a catalyst.  
Materials:

- 430 g. (0.5 mol) Polypropylene (M.W. 860)  
5 59 g. (0.5 mol+25% xs) Phenol (7.4 g. from the phenolate complex)  
10 g.  $\text{BF}_3 \cdot 2\text{C}_6\text{H}_5\text{OH}$  26%  $\text{BF}_3$  (2.6 g.  $\text{BF}_3$  and 7.4 g. phenol)

10 The  $\text{BF}_3$  content of the catalyst was 0.5% of the total amount of reactants.

The apparatus was the same as in Example 1, and the same procedure was followed. The mixture was heated 2 hours at  $80^\circ\text{C}$ ., 4 hours at  $100^\circ\text{C}$ ., 1 hour at  $150^\circ\text{C}$ . and 15 minutes at  $220^\circ\text{C}$ . After cooling down it was dissolved in toluene and washed with hot water, to remove the  $\text{BF}_3$  and unreacted phenol, until neutral to litmus. The mixture was stripped under vacuum (10 mm) at  $180^\circ\text{C}$ . and the clear, brown viscous material gave the following analysis:

	Theory	Found
Active Hydrogen	1.05 m moles $\text{CH}_4/\text{g}$	0.75 m moles $\text{CH}_4/\text{g}$

25 Chromatographic clay separation=46.9% yield.

#### EXAMPLE 3

30 This example illustrates the alkylation of phenol with polypropylene with 1.5%  $\text{BF}_3$  as a catalyst. A different procedure from that in the previous example was used, as far as the time of reaction and the washing of the mixture is concerned.  
Materials:

- 35 1600 g. (2 mols) Polypropylene (M.W.=800)  
235 g. (2 mols+25% xs) Phenol (78.5 g. from the phenolate complex)  
40 106 g.  $\text{BF}_3 \cdot 2\text{C}_6\text{H}_5\text{OH}$  26%  $\text{BF}_3$  (27.5 g.  $\text{BF}_3$  and 78.5 g. phenol)

The  $\text{BF}_3$  content of the catalyst was 1.5% of the total amount of the reactants.

45 The apparatus consisted of a 5 liter, four-necked reaction flask equipped with a mechanical stirrer, reflux condenser, thermometer and dropping funnel.

The polypropylene and phenol were charged to the flask at a temperature of  $60^\circ\text{C}$ ., and the  $\text{BF}_3 \cdot 2\text{C}_6\text{H}_5\text{OH}$  complex (27.5 g  $\text{BF}_3$  and 78.5 g phenol) was added dropwise through the dropping funnel during continuous stirring. The reaction mixture was heated up to  $150^\circ\text{C}$  slowly, because of the possibility of foaming, and held at that temperature for 4 hours. After cooling down to  $90^\circ\text{C}$  1 litre of toluene and 50 cc of butyl alcohol were added (for better separation) and the mixture was washed initially with 2 liters of hot water

to remove the  $\text{BF}_3$  and the unreacted phenol, secondly with a 5% wt. aqueous KOH solution to remove the remaining traces of phenol, thirdly, with a 5% wt. aqueous HCl acid solution to neutralize the remaining KOH and finally many times with hot water until neutral to litmus. The mixture was filtered through filter paper and stripped under vacuum (5—10 mm) at  $180^\circ\text{C}$ . The product was a clear, brown viscous material which gave the following analysis:

	Theory	Found	
Active Hydrogen	1.11 m moles $\text{CH}_4/\text{g}$	0.83 m moles $\text{CH}_4/\text{g}$	70
Yield based on the Active hydrogen analysis	=74.8%		
Chromatographic clay separation	=76.37%		75

#### EXAMPLE 4

This example illustrates an alkylation of phenol with polypropylene following the same procedure as Example 3 but with a ratio of polypropylene to phenol of 1 to 0.85 mols. Materials:

- 1600 g. (2 mols) Polypropylene (M.W.=800)  
156.6 g. (1.7 mols) Phenol (74.6 g. from the phenolate complex)  
101 g.  $\text{BF}_3 \cdot 2\text{C}_6\text{H}_5\text{OH}$  26%  $\text{BF}_3$  (26.4 g.  $\text{BF}_3$  and 74.6 g. phenol)

The  $\text{BF}_3$  content of the catalyst was 1.5% of the total amount of the reactants.

The apparatus and the procedure were the same as in Example 3. The analysis of the product gave the following results:

	Theory	Found	
Active Hydrogen	1.11 m moles $\text{CH}_4/\text{g}$	0.65 m moles $\text{CH}_4/\text{g}$	95
Yield based on the Active Hydrogen analysis	=60.0%		
Chromatographic clay separation	=62.9%		

#### EXAMPLE 5

100 This example illustrates the alkylation of phenol with polybutylene which gives polybutenylphenol, using 1.5%  $\text{BF}_3$  as a catalyst. Materials:

- 1900 g. (2 mols) Polybutylene (M.W.=950)  
235 g. (2 mols+25% xs) Phenol (91 g. from the phenolate complex)  
123 g.  $\text{BF}_3 \cdot 2\text{C}_6\text{H}_5\text{OH}$  26%  $\text{BF}_3$  (32 g.  $\text{BF}_3$  and 91 g. phenol)

The  $\text{BF}_3$  content of the catalyst was 1.5% of the total amount of reactants.

The same procedure was followed as in Example 3. The product, a clear, brown viscous material, gave the following analysis: 115



	Theory	Found
Active Hydrogen	0.99 m moles	0.79 m moles
	CH <sub>4</sub> /g	CH <sub>4</sub> /g
Chromatographic	clay separation=50.2%	
5 yield.		

## EXAMPLE 6

This example illustrates an alkylation of phenol with polypropylene similar to Example 3, but on a large scale.

## 10 Materials:

	34 kg (42.5 mols) Polypropylene (M.W.=800)
	5 kg (42.5 mols+25% xs) Phenol (1.7 kg from the phenolate complex)
15	2.25 kg BF <sub>3</sub> ·2C <sub>6</sub> H <sub>5</sub> OH 26% BF <sub>3</sub> (585 g. BF <sub>3</sub> )

The BF<sub>3</sub> content of the catalyst was 1.5% of the total amount of reactants.

20	The above listed quantities were charged into a 30 gallon Pfaulder kettle. The mixture was heated and stirred for 4 hours at 300°F., then it was cooled down to 175°F. and 14 kg toluene, 3.4 kg butyl alcohol and 34 kg distilled water were added to wash out the BF <sub>3</sub> and the unreacted phenol. After that the mixture in the kettle was washed with 5% aqueous KOH solution to remove any remaining phenol, then with 5% wt. aqueous HCl solution to neutralize the unreacted KOH and finally 3 times with distilled water until neutral to litmus at a temperature in the vicinity of 150°F.
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35	The washed mixture was filtered through a plate filter using 3/4 lb. of Hy-Flo (registered Trade Mark) filter aid (Diatomaceous earth) and then the toluene and butyl alcohol were stripped off under vacuum (30—40 mm) at 300°F. The product, a clear, brown, viscous oil, gave the following analysis:
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	Theory	Found
40 Active Hydrogen	1.11 m moles	0.85 m moles
	CH <sub>4</sub> /g	CH <sub>4</sub> /g
	Yield based on the Active Hydrogen analysis=76.5%	
45	Chromatographic clay separation=73.5% yield	

50	In this preparation a different method, using NH <sub>3</sub> gas and steam distillation, was applied to remove the excess of BF <sub>3</sub> and unreacted phenol after the reaction of polypropylene with phenol as illustrated in the first part of this example.
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55	In a 3 liter, 4-necked flask, equipped with a stirrer, thermometer, condenser and an inlet tube for the NH <sub>3</sub> gas, one kg of material (taken from the kettle just before washing) was placed in the flask. The temperature was raised up to 100°C. and while stirring, NH <sub>3</sub> gas passed for 2 hours. The mixture turned hazy because the ammonium salt of BF <sub>3</sub> was formed, according to the reaction: BF <sub>3</sub> +
60	

NH<sub>3</sub>→BF<sub>3</sub>—NH<sub>3</sub>. The mixture was filtered to remove the BF<sub>3</sub> ammonium salt, and it was steam distilled with superheated steam (180—200°C) to remove the unreacted phenol.

This method of removing the BF<sub>3</sub> and unreacted phenol gave results very close to the previous method.

Analysis:

	Theory	Found
Active Hydrogen	1.11 m moles	0.82 m moles
	CH <sub>4</sub> /g	CH <sub>4</sub> /g
Yield based on the Active Hydrogen analysis=84%		

## EXAMPLE 7

This example illustrates alkylation of phenol similar to Example 3, but using a higher molecular weight polypropylene.

Materials:

	2240 g (2 mols) Polypropylene (M.W.=1120)
	235 g. (2 mols+25% xs) Phenol (106 g. from the phenolate complex)
	143 g. BF <sub>3</sub> ·2C <sub>6</sub> H <sub>5</sub> OH 26% BF <sub>3</sub> (37 g. BF <sub>3</sub> and 106 g. phenol)

The BF<sub>3</sub> content of the catalyst was 1.5% of the total amount of reactants.

The apparatus was the same as in Example 3. The same procedure was followed. During the stripping about 50 g. of light ends of polypropylene came out. The product, a clear, brown, viscous oil, gave the following analysis:

	Theory	Found
Active Hydrogen	0.817 m moles	0.59 m moles
	CH <sub>4</sub> /g	CH <sub>4</sub> /g
Chromatographic	clay separation=54.6%	
95 yield.		

The polypropenylphenol and polybutenylphenol prepared and described above were tested in two bench tests: "Sulfuric Acid Neutralization Test"<sup>1</sup> and "Pyruvic Acid Dispersion Test"<sup>2</sup>. These tests are designed for evaluating detergents for use in engines operating on sulfur-containing fuels.

<sup>1</sup>This method gives a measure of the ability of detergent additives to neutralize strong acids formed in engines operating on sulfur-containing fuels. H<sub>2</sub>SO<sub>4</sub> is mixed with a heated blend of the additive and the oil. A solution of this is formed in isooctane which is then centrifuged to separate insolubles. The optical density of the clear solution is then measured. From this value of the optical density of the original additive blend diluted to a corresponding amount with isooctane is subtracted. The difference gives the optical density of the dispersed H<sub>2</sub>SO<sub>4</sub> reaction products. The optical density of an acetone extraction of the isooctane-oil solution is then determined. The

- average optical density of the oil-isooctane solution is expressed as the optical density of the dispersed  $H_2SO_4$  reaction product. The average density of the acetone solution is expressed as the optical density of the non-dispersed  $H_2SO_4$  reaction products. The total of these values or either one alone is used in the evaluation of detergent additives.
- <sup>2</sup>This method gives a measure of the dispersant value of additives and serves to predict the performance of detergent additives in engines operating on low sulfur content fuels. When used in combination with the neutralization of  $H_2SO_4$  bench test procedures it serves to predict the performance of detergent additives in engines operating on high sulfur content fuels. Pyruvic acids is mixed with a heated blend of the additive and the oil. The mixture is diluted with benzene and centrifuged to separate insolubles. The insolubles are dissolved in acetone. The optical density of the oil-benzene solution gives the total amount of color. From this value the optical density of the initial additive blend diluted with benzene to a corresponding amount is subtracted. This corrected value is expressed as the optical density of the dispersed pyruvic acid polymer. The optical density of the acetone solution is expressed as the optical density of the non-dispersed pyruvic acid polymer. These values are used in the evaluation of the detergent additives.
- The polypropenylphenol and polybutenylphenol gave the following results in Pyruvic and Sulfuric Acid bench tests in a 3% blend, in comparison with a blank test without additive.
- Rating: The higher the value of the Pyruvic Acid test results the better the additive. The lower the value of the Sulfuric Acid test results the better the additive.

Table I

	Blends	Pyruvic Acid	Sulfuric Acid
45	3% Polypropenylphenol (Example 6) and 1% corrosion inhibitor <sup>2</sup> in base stock <sup>1</sup>	79.9%	0.029
	3% Polybutenylphenol (Example 5) and 1% corrosion inhibitor in base stock	83.3%	0.053
50	1% corrosion inhibitor in base stock	58.6%	0.102

<sup>2</sup>zinc dihexyl phosphorodithionate

(99°C)

<sup>1</sup>S.A.E. 30 grade mineral oil with an S.U.V.210°F. of 64.1.

- These tests indicate the substantial improvements in lubricants which can be obtained by the use of the novel compositions of matter of this invention. In particular, the excellent dispersant properties of these high molecular weight compositions should be noted.
- The additives of this invention can be used in any one of a wide variety of oils of lubricating viscosity, such as natural, refined or synthetic oils, or in blends of such oils.
- These oils may be prepared with or without auxiliary conventional additives such as: oiliness and extreme pressure agents; corrosion, oxidation and rust inhibitors; viscosity index improving agents; coloring agents and auxiliary detergents.
- WHAT WE CLAIM IS:—
1. A hydrocarbon composition which comprises a hydrocarbon vehicle and from 0.05 to 25% by weight of the vehicle of a polyalkenyl substituted phenol produced by reacting a phenolic compound with a polyalkylene compound having a molecular weight of from 600 to 3000, in the presence of a boron trifluoride complex catalyst.
  2. A composition according to claim 1 in which the boron trifluoride complex catalyst is a boron trifluoride phenolate complex catalyst.
  3. A composition according to claim 1 or 2 in which the phenolic compound is phenol.
  4. A composition according to claim 2 or 3 in which the boron trifluoride phenolate complex has the formula  $BF_3 \cdot 2C_6H_5OH$ .
  5. A composition according to any of claims 1 to 4 in which the mol ratio of the phenolic compound to polyalkylene compound is 1:1 to 1.5:1.
  6. A composition according to any of claims 1 to 5 in which the polyalkylene compound is polypropylene.
  7. A composition according to any of claims 1 to 6 in which the polyalkylene compound is polybutene.
  8. A composition according to any of claims 1 to 7 in which the reaction is carried out at a temperature of from 80° to 250°C.

9. A hydrocarbon composition according to any of the preceding claims substantially as herein described with reference to any of the examples.

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